Response of Water Chemistry and Young-of-Year Brook Trout to Channel and Watershed Liming in Streams Showing Lagging Recovery from Acidic Deposition

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Abstract Reductions in sulfur emissions have initiated chemical recovery of surface waters impacted by acidic deposition in the Adirondack region of New York State. However, acidified streams remain common in the region, which limits recovery of brook trout (Salvelinus fontinalis) populations. To investigate liming as a method to accelerate recovery of brook trout, the channels of two acidified streams were limed annually from 2012 to 2015, and an entire watershed of a third acidified tributary was limed by helicopter in 2013. Stream flow, water

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B. P. Baldigo e-mail: bbaldigo@usgs.gov chemistry, and density of young-of-year (YOY) brook trout were measured in limed streams, an untreated acidified stream, and a buffered reference stream. Lime additions increased pH and acid-neutralizing capacity and decreased inorganic monomeric aluminum concentrations to less than 2.0 μmol/L, the minimum concentration at which in situ brook trout mortality has been documented. However, of the two channel-limed streams, only stream T8 showed a significant response $(P<0.01)$ in YOY density, increasing from a mean of 0.4 fish/ m^2 before liming to 2.7 fish/ m^2 after liming. No YOY brook trout response was observed in the stream within the limed watershed. Groundwater inputs to streams were identified by relative differences in temperature and concentrations of silica and sodium. YOY brook trout densities increased only in the channellimed stream (T8) with suitable groundwater inputs for fall spawning and a summer nursery. Results suggest that targeted liming of acidified streams with the necessary groundwater habitat could be beneficial in accelerating recovery of brook trout populations.

Keywords Stream liming . Channel . Watershed . Brook trout . Groundwater

1 Introduction

Brook trout (Salvelinus fontinalis) historically inhabited numerous lakes and streams in the Adirondack Mountain region of New York, but many populations in poorly buffered watersheds were lost during the 1970s and 1980s due to acidification of surface waters by acid deposition (Schofield [1976](#page-13-0)). Regulatory actions have decreased emissions of sulfur, stimulating the recovery of surface water chemistry, but numerous lakes and streams remain acidified to varying degrees within the region (Driscoll et al. [2016;](#page-13-0) Lawrence et al. [2016](#page-13-0)). Gradual chemical recovery has delayed the recovery of Adirondack fish populations (Baldigo et al. [2007](#page-13-0); Driscoll et al. [2016](#page-13-0)). Many lakes in the region can now support brook trout populations by stocking; however, the re-establishment of naturally reproducing populations is likely limited by chronic and episodic acidification of tributaries that provide critical spawning and nursery habitat (Josephson et al. [2014](#page-13-0)).

The extent to which lake and stream surface waters are impacted by acidic deposition on the Adirondack landscape (and other glaciated upland regions) is largely dependent upon the presence or absence of till deposited through glaciation (Driscoll and Newton [1985](#page-13-0)). Till thickness is an important control over the degree of acid buffering that can be achieved, but where till is thin or absent, acid-buffering is more dependent on soils. Soils that develop with little or no influence of underlying till tend to have naturally low acid-buffering capacity (Sullivan et al. [2006\)](#page-14-0). Till thickness can vary widely within the region and results in watersheds in close proximity that exhibit large differences in acid-buffering capacity. Stream acidification is also tied to changes in flow that can cause large temporal variations in the degree of acidification (Lawrence et al. [2008\)](#page-13-0).

The delayed recovery of surface waters is largely due to depletion of calcium (Ca) from soils, which has reduced the acid-buffering capacity of watersheds where Ca availability was naturally low (Driscoll et al. [2001\)](#page-13-0). The loss of watershed buffering capacity has increased the susceptibility of surface waters to acidification, thereby slowing recovery from acidification, even as acidic deposition decreases in the region. Restoration of available Ca in the soil is needed to increase acid-buffering capacity and improve ecosystem function through its role as a nutrient. However, replenishment of ecosystemavailable Ca is a slow process dependent on the weathering of rocks. Soil monitoring data have yet to show increases in Ca availability in response to declining deposition, while decreases in soil Ca that were commonly reported in the past appear to have stabilized throughout the northeastern U.S. (Lawrence et al. [2015](#page-13-0)).

One possible approach to accelerate the chemical and biological recovery of streams is the application of lime (ground limestone) to bolster acid neutralization and increase Ca availability for nutrient utilization. Various liming approaches have been used for over three decades in both Europe and North America, with the objective of reducing or eliminating further damage until the necessary reductions in acidic deposition levels were implemented (Lawrence et al. [2016](#page-13-0)). With large decreases in acidic deposition in the northeastern U.S.A over the past two decades ([http://nadp.slh.wisc.edu/;](http://nadp.slh.wisc.edu/) accessed June 1, 2018) and soil Ca levels appearing to stabilize, liming can now be considered as a method to accelerate replenishment of lost Ca rather than relying solely on mineral weathering to increase Ca availability and buffering capacity in streams.

The two general approaches for liming-acidified streams involve direct addition to the stream channel (Downey et al. [1994;](#page-13-0) Clayton et al. [1998](#page-13-0)) and terrestrial liming of parts or all of the stream drainage (Driscoll et al. [1996](#page-13-0); Newton et al. [1996](#page-13-0)). These liming experiments have demonstrated that both methods can neutralize the acidity of streams, but questions remain regarding effectiveness over the full range of flow conditions that occur in streams, the seasonal timing of the application, and the effect on reproductive success of high-value fish species, which are important to sustaining recovery goals.

Accordingly, an interdisciplinary investigation was initiated to evaluate the effects of channel and watershed liming practices to accelerate chemical and biological recovery of tributaries to Honnedaga Lake in the western Adirondack region of New York, where most tributaries remain too acidic to support brook trout reproduction or to provide summer habitat for young-of-year (YOY) brook trout (Josephson et al. [2014](#page-13-0)). Lime was applied directly to the channel of two acidified tributaries and by helicopter to the entire watershed of a third acidified tributary. The objectives of the study were to:

- 1. Measure water chemistry monthly and during highflow episodes in treated and untreated tributaries to assess the chemical effects of liming,
- 2. Determine the response of fall spawning by adult brook trout and the summer use by YOY brook trout in treated and untreated tributaries, and
- 3. Identify tributary characteristics and liming techniques that yielded the strongest water chemistry and brook trout population responses to provide

management options for targeted mitigation of streams that exhibit lagging recovery from acidic deposition effects.

2 Methods

2.1 Study Area

Honnedaga Lake is a large (312 ha), deep (56 m), highelevated (701 m) water body located in the southwestern Adirondack region in New York (Fig. [1\)](#page-3-0). The lake supports the Honnedaga brook trout genetic strain, one of seven remaining heritage strains identified in New York State (Perkins et al. [1993\)](#page-13-0). Honnedaga Lake has been classified as a thin-till drainage lake that is highly susceptible to acid deposition (Baker et al. [1990\)](#page-13-0). Due to its location in the southwestern Adirondacks, the watershed has received high levels of acidic deposition for decades, although wet deposition of sulfur in 2015 was about 25% of that observed in 1980 ([http://nadp.slh.](http://nadp.slh.wisc.edu/) [wisc.edu/;](http://nadp.slh.wisc.edu/) accessed June 1, 2018). The Honnedaga Lake watershed is naturally low in available Ca due to slowly weathering geological substrate and thin soils that are highly leached by an average of 1.27 m of precipitation per year (Josephson et al. [2014](#page-13-0)). During winter, snow accumulation usually surpasses 1 m, and often produces high stream flows during spring snowmelt events in March and April.

Anecdotal information suggests that Honnedaga Lake was historically a brook trout monoculture. Stocking of non-native fish in the 1890s resulted in the establishment of reproducing populations of lake trout (Salvelinus namaycush), round whitefish (Prosopium cylindraceum), creek chub (Semotilus atromaculatus), and white sucker (Catostomus commersonii), but all of these species disappeared from the lake between 1930 and 1955, leaving only brook trout extant (Josephson et al. [2014](#page-13-0)). By 1960, surface waters of the lake were chronically acidified (pH < 5.0) and corresponding inorganic monomeric aluminum (Al_{im}) concentrations often exceeded the 2.0-μmol/L lethal threshold for brook trout (Baldigo et al. [2007](#page-13-0)). Yet during this period of chronic acidification, brook trout were able to sustain populations in several small tributaries that received wellbuffered groundwater (Kraft [2019](#page-13-0)). As a result of the 1990 Clean Air Act Amendments and other regulations, acidification of Honnedaga Lake began to decrease,

which initiated recovery of brook trout within the lake (Kraft [2019](#page-13-0)). However, chronic acidification of most tributaries still adversely affects YOY survival and recruitment and continues to limit recovery of the brook trout metapopulation within the Honnedaga Lake drainage (Josephson et al. [2014\)](#page-13-0).

2.2 Study Design

In a prior study, Josephson et al. [\(2014\)](#page-13-0) sampled water chemistry in all 23 tributary streams to Honnedaga Lake weekly from June–August over a 3-year period (2008– 2010). Based on chemical analysis of those samples, five tributaries were selected for this study to provide a range in acid-base chemistry (Fig. [1](#page-3-0)). Using the same stream identification codes as Josephson et al. [\(2014\)](#page-13-0), T6 and T8 were selected for direct liming of stream channels, T16 for whole-watershed liming, and T20 and T24 to serve as untreated reference streams.

Flow was monitored in the five streams at gages installed near the point of discharge into the lake above the maximum lake level. Flow data used in this analysis covered the period from 1/1/2012 through 12/31/2015. Stream stage measurements were recorded at 15-min intervals throughout the year using Druck pressure transducers. Discharge measurements were made using a handheld acoustic Doppler velocimeter. Stage was converted to discharge using U.S. Geological Survey (USGS) methods described in Rantz ([1982](#page-13-0)) as guidance. Discharge for periods that exceeded the greatest measured discharge was estimated using areal comparisons of peak-runoff rates at nearby gages. Gage numbers for each flow measurement site (listed in Table [1](#page-3-0)) can be used to access flow data available from the USGS National Water Information System (U.S. Geological Survey [2018](#page-14-0)). At each stream gage, water-chemistry samples were collected manually by filling a bottle at stream side after three rinses, for the period from May 2011 to September 2015 at approximately monthly intervals, and during high-flow episodes from May through November each year using stage-activated autosamplers that collected an individual sample when triggered by a preset change in stage. The pre-treatment monitoring period for stream water sampling extended from 5/16/2011 to 7/9/2012 for the two streams with limed channels (T6 and T8), and from 5/16/2011 to 9/25/2013 for the stream within the limed watershed (T16). For comparison purposes, the pre-treatment period for reference stream T20 was the same as for T6 and Fig. 1 Location of study tributaries (T6, T8, T16, T20, T24). Watershed areas are delineated by shaded areas

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Base from ESRI World Topographic Map; NAD 1983 UTM Zone18N
Stream network from USGS StreamStats 2017

T8, and the pre-treatment period for reference stream T24 was the same as for T16. To provide an understanding of local treatment effects in the two lime addition streams, additional water-chemistry samples were collected in T6 and T8 at locations immediately above the point of lime additions (site T6A and T8A, respectively) on an approximately monthly basis from 5/14/2012 to 9/21/2015.

All stream water samples were analyzed for pH, acidneutralizing capacity (ANC) and total monomeric and organic monomeric Al (aluminum), sodium (Na), and silicon (Si) by the USGS New York Water Science Center Soil and Low-Ionic-Strength Water Quality Laboratory (Troy, NY). Standard operating procedures for these analyses are available online ([https://www.](https://www.sciencebase.gov/catalog/item/55ca2fd6e4b08400b1fdb88f) [sciencebase.gov/catalog/item/55ca2fd6e4b08400b1](https://www.sciencebase.gov/catalog/item/55ca2fd6e4b08400b1fdb88f)

[fdb88f;](https://www.sciencebase.gov/catalog/item/55ca2fd6e4b08400b1fdb88f) accessed April 18, 2018). Inorganic monomeric aluminum (Al_{im}) was determined by subtracting concentrations of organic monomeric Al (Alom) from total monomeric Al (Altm). All stream chemistry data are available from the USGS National Water Information System (U.S. Geological Survey [2017](#page-14-0)) using site codes listed in Table 1, except site T6A (site code 0134277118) and T6B (site code 0134277120).

2.3 Lime Treatments

In-channel Lime Application Pelletized limestone (ground to 98% pass through a 20 mesh or 841 μm, screen before pelletization) was poured from 50-lb (22.7 kg) bags directly into the channels of T6 and T8 four times according to the schedule and doses listed in

Site ID	NWIS ID^a	Watershed area (ha)	Treatment	Treatment dates	Mass (Mg) added lime	Mass (Mg) added Ca
T ₂₀	0134277123	18	Untreated			
T8	0134277121	37	Channel liming	$7/12/12$; $6/19/13$; $3/5/14$; 6/16/15	4.5	1.38
T6	0134277119 248		Channel liming	$7/12/12$; $6/19/13$; $2/28/14$; 6/16/15	10	3.04
T ₂₄	0134277112	25	Untreated			
T ₁₆	0134277114	30	Watershed liming	$10/1/13 - 10/3/13$	136	$1.4^{\rm b}$

Table 1 Site and USGS gage numbers (NWIS codes), watershed areas, and treatment information for the five study streams

^a NWIS ID refers to USGS National Water Information System site identification number

 b Ca dose for watershed T16 is listed as Mg Ca ha⁻¹</sup>

Table [1](#page-3-0). On a mass basis, the Ca concentration of the lime ranged from 30 to 34% and the concentration of magnesium (Mg) in the lime ranged from 1.3 to 3.3%. The selected dose was determined using the West Virginia Formula (Clayton et al. [1998](#page-13-0)) which is based on watershed area, and the Clayton Formula (Clayton et al. [1998](#page-13-0)) based on watershed area and mean stream pH for channel applications of lime. The dosage determined by the two methods was averaged and then doubled for each application because the tributaries had been impacted by acidification for several decades. T6 had received a one-time application of 4.5 megagrams (Mg) of lime in fall 2010 prior to the initiation of this study. Lime was applied approximately 1370 m upstream of the highest lake level in T6 and 150 m upstream of the highest lake level in T8.

Watershed Lime Application Lime (30% Ca by mass, < 2% Mg by mass), ground for 100% pass through a 20 mesh, or 841-μm screen, was distributed in pelletized form $(100\%$ pass through a 4 mesh, or 4760 - μ m screen) by helicopter over the T16 (136,078 kg one application) watershed in the mid-stages of fall leaf drop, 10/1/2013– 10/3/2013 (Table [1\)](#page-3-0). To equalize lime distribution, all areas of the watershed received two passes by the helicopter. Twenty collection sheets distributed on the ground throughout the watershed were used to quantify variability in the distribution of limestone pellets. The coefficient of variation for the mass of pellets collected by the 20 sheets was 41%. The single treatment added 1.4 mg Ca ha⁻¹, which falls between the 2.8 mg Ca ha⁻¹ added to Woods Lake watershed in a liming experiment conducted in the Adirondack region (Driscoll et al. [1996](#page-13-0)) and the 0.85 mg Ca ha^{-1} added as wollastonite to watershed 1 at the Hubbard Brook Experimental Forest, New Hampshire (Cho et al. [2010\)](#page-13-0). The T16 watershed dose was one-half that applied to the Woods Lake watershed in 1989, when atmospheric sulfate $(SO₄²)$ deposition was approximately double the rate in 2011 (<http://nadp.slh.wisc.edu/>; accessed June 1, 2018).

2.4 Assessment of Groundwater Inputs

Discharged groundwater is defined here as water that enters the stream channel after passing through subsoil flow paths within till and bedrock. Groundwater discharge was evaluated because it could influence stream water chemistry and the effectiveness of liming due to

variable chemical inputs. Concentration measurements of Si and Na were used for this purpose because in Adirondack lakes, concentrations of these constituents are indicative of relative differences in flow paths among watersheds (Newton et al. [1987](#page-13-0); Peters and Driscoll [1987\)](#page-13-0). For this analysis, pre-treatment samples collected at the gages during summer baseflow (7/19/ 2011, 8/1/2011, and 7/9/2012) were used to (1) avoid possible contamination from liming and (2) maximize the chemical expression of subsoil flow paths where they exist.

Water temperature was also used to evaluate relative differences in flow paths among the watersheds. Stream water temperatures were recorded at 15-min intervals at each of the stream gage locations using Campbell Scientific CS-107 temperature probes. All stream temperature data are available from the USGS National Water Information System (U.S. Geological Survey [2018\)](#page-14-0). Temperature data converted to mean daily averages for July and August 2013–2015 were selected for the analysis to reflect the period when subsoil flow paths were likely to have their maximum influence. Missing values in the electronic record for T24 for the period 8/10/2015 to 8/31/2015 were estimated by linear regression using the average daily values for T8 and T16 for the same period.

2.5 Brook Trout Population Assessments

Summer Electrofishing Surveys Backpack electrofishing surveys were conducted annually in the study streams in early August between 2009 and 2011 using a single pass and in early August between 2012 and 2015 using three passes. All brook trout were collected using a battery-powered, pulsed direct current electrofishing unit (Advanced Backpack AbP-3 Unit; ETS Electrofishing, LLC). Survey reaches began at the tributary-lake confluence and continued upstream between 10 and 35 m. Fish were surveyed in an additional reach upstream from Honnedaga Lake, and below the lime application sites, in T6.2 (500 m above lake confluence and site T6.1) and T8.2 (200 m above lake confluence and site T8.1) (Fig. [1\)](#page-3-0). For all surveys, blocking nets were placed at the downstream and upstream boundaries of each reach for all electrofishing passes. The total length and average width of channels were used to calculate the total sampled area of each survey reach. The lengths of all fish were recorded to the nearest millimeter and most fish were released back into

the study reach. A total of 43 brook trout, ranging from 38 to 137 mm were collected from T6, T8, and T20 in August 2016 and euthanized with MS-222. The ages of these 43 fish were determined from otoliths. The results from all electrofishing surveys are summarized herein and the raw data are available from Cornell University by permission from Dr. Cliff Kraft who is responsible for their collection, management, and archiving.

Fall Trap Net Surveys Relative abundance of the adult spawning stock was determined by trap net data collected each fall between 2008 and 2014. The numbers of adult brook trout caught in any given year (n) produced year class $(n + 1)$; thus, fall trap net catches from 2008 to 2014 contributed to brook trout year classes 2009 to 2015. Trap net surveys were conducted at the same six locations during the same week of October every year to record the number of sexually mature female and male brook trout. Four net sites were in the vicinity of tributaries and shoals with known brook trout spawning and the other sites were located (1) on the shoreline opposite T24 and (2) 300 m west of T6 (at the mouth of a small tributary T4) (Fig. [1\)](#page-3-0). Relative abundance was represented as the number of adults captured per trap net night.

Fall Redd Surveys The amount of spawning by females in the lake was assessed from annual redd surveys conducted during late October to early November between 2008 and 2014. The number of redds was determined by slowly motoring a boat around the entire shoreline perimeter while two observers scanned the water and counted redds on four shoals. Additionally, six tributaries including T6, T8, T16, T20, T24, T4, and the outlet were surveyed for spawning brook trout and redds each year during the same period (Fig. [1](#page-3-0)).

Data Analysis The catch of YOY brook trout for singlepass surveys was expressed as the number of fish per square meter (hereafter density). Population estimates were determined from the three-pass surveys using a maximum likelihood population estimator and standardized by arae to produce density estimates (Van Deventer and Platts [1985](#page-14-0)). The relation between single-pass catch density and the three-pass depletion density estimates was assessed using linear regression. A strong positive relation was present between the single-pass density and three-pass density estimates (linear regression; R^2 = 0.92, $P < 0.001$), which indicated that the single-pass catch rates were a representative indicator of total population (and YOY) density in these small streams. Therefore, the single-pass catch rate of YOY brook trout (number/ $m²$) was used as the response variable to evaluate the biological effects of the channel and watershed lime applications.

A paired before-after control-impact (BACI) experimental design was used to examine the net response of YOY brook trout to channel lime applications (pre-lime 2009 to 2012 and post-lime 2013 to 2015) and to watershed lime application (pre-lime 2009 to 2013 and post-lime 2014 to 2015) relative to untreated control (i.e., reference) sites. A BACI design is appropriate because it assesses the same response variable at a treated and reference site before and after an impact (i.e., treatment), and therefore can separate the direct effects caused by a treatment from widespread changes caused by climatic variations (e.g., unusual precipitation or temperature events) (Smith [2002](#page-14-0)). The BACI design was analyzed using a linear mixed model with the fixed effects "treatment" (reference or impact) and "period" (before or after), the interaction term "treatment x period", and the random effect "year" using the nlme package in R (R-Core team [2016](#page-13-0)). In a BACI design, the main effects are not of interest and the significance of the interaction term serves as a test of the null hypothesis of no differential change between reference (control) and impact sites following some type of manipulation. An estimate of the BACI contrast (net effect of the treatment) was calculated for each response variable as the change (before-after) in the mean at the reference site minus the change in the mean at the treatment site.

3 Results

3.1 Reference and Pre-treatment pH, ANC, and Al_{im}

Stream chemistry fluctuated widely in untreated T20 over the sampling period (5/16/2011–9/21/2015) in response to seasonal fluctuations in flow (Fig. [2\)](#page-6-0). Values of ANC increased during low summer flows and decreased during high spring flows, but rarely became severely acidic. Values of pH ranged from slightly less than 5.0 to slightly greater than 7.0 and ANC ranged from slightly less than 0.0 to slightly greater than 200 meq L^{-1} . Most Al_{im} concentrations fell below the 2.0-μmol L^{-1} threshold, above which we expect to see significant biological impact (Baldigo et al. [2007](#page-13-0)). However, during high-flow events, the Al_{im}

Fig. 2 Measurements of pH, ANC, and Al_{im} from all water samples collected at T20. Circles indicate monthly manual samples, triangles indicate autosamples triggered by flow events, and gray shading indicates AI_{im} levels that are not harmful to resident brook trout (2011–2015)

concentrations were elevated, with the highest concentration sample exceeding 5.0 µmol L^{-1} (Fig. 2). Based on the range of stream chemistry expressed by T20, this watershed was designated as rarely acidic for this analysis. Linear regression indicated no trends with time $(P > 0.10)$ in the chemical measurements of T20 over the sampling period. In contrast, stream chemistry in untreated reference T24 remained severely acidified throughout the study period with pH values rarely exceeding 4.7, ANC values negative in nearly all samples, and Al_{im} ranging from 4.0 to 13 µmol L^{-1} (Fig. 3). Therefore, T24 was designated as chronically acidic for this analysis. The chemical measurements for T24 did not exhibit trends with time $(P > 0.10)$. Measurements of pH, ANC, and Al_{im} in T16 during the pretreatment period were comparable with those in T24 during the same period (Fig. 3), so T16 was also designated as chronically acidic.

Stream chemistry in T8 during the pre-treatment period varied from well-neutralized to severely acidified (Fig. [4\)](#page-7-0). Values of pH approached 6.5, but also decreased to 4.8, ANC ranged from -13 to 117 meq L⁻¹, and Al_{im} exceeded 2.0 µmol L^{-1} in 9 of 26 samples, with one sample reaching 5.7 μ mol L⁻¹. Based on the pretreatment stream chemistry, T8 was designated as

Fig. 3 Measurements of pH, ANC, and Alim from all water samples collected in T24 (reference stream shown in red) and T16 (stream in the limed watershed shown in blue). Circles indicate monthly manual samples, triangles indicate autosamples triggered by flow events, and gray shading indicates Alim levels that are not harmful to resident brook trout (2011–2015). The vertical red line indicates the date when lime was added to the T16 watershed

episodically acidic. Pre-treatment stream chemistry in T6 showed similar fluctuations to those observed in T8 and was also designated as episodically acidic. Values of pH in T6 reached as high as 5.8, and as low as 4.7, ANC ranged from -14 to 128 meq L⁻¹, and Al_{im} exceeded 2.0 μmol L^{-1} in 11 of 26 samples, with one sample reaching 4.7 μ mol L⁻¹ (Fig. [5](#page-7-0)).

3.2 Measurements of Temperature and Concentrations of Si and Na

Mean water temperatures during July and August 2013– 2015 did not significantly differ among T16, T20, and T24 ($P > 0.10$; Tukey multiple comparison test), varying from 13.0 to 13.4 °C. The mean temperature in T8 of 14.1 °C was about 1 °C higher ($P < 0.05$) than these other streams (Table [2](#page-8-0)). Maximum temperatures of these four streams ranged between 17.2 and 18.1 °C (Table [2\)](#page-8-0). The temperatures at T6, however, were approximately 3 to 4 °C warmer ($P < 0.01$) than at the other four study streams, with a mean value of 17.1 °C and a maximum of 22.3 °C. Concentrations of Si and Na were similar in T20 and T8 ($P > 0.10$; Tukey multiple comparison test),

Fig. 4 Measurements of pH, ANC, and Alim of all water samples collected at T8. Circles indicate manual samples collected monthly, triangles indicate autosamples triggered by flow events, green diamonds indicate data from T8A, a site upstream of the gage, vertical red lines indicate when lime was added, and gray shading indicates Al_{im} levels that are not harmful to resident brook trout. Note: an ANC value of 1650 meq L^{-1} (not shown) was measured on 10/17/2012

Fig. 5 Measurements of pH, ANC, and Al_{im} of all water samples collected at T6. Circles indicate monthly manual samples, triangles indicate autosamples triggered by flow events, green diamonds indicate data from T6, a site upstream of the gage, vertical red lines indicate when lime was added, and gray shading indicates Alim levels that are not harmful to resident brook trout (2011–2015)

and significantly higher ($P < 0.05$) than in T6, T16, and T24 by at least a factor of two (Table [2\)](#page-8-0). Concentrations of Si and Na were somewhat higher in T16 than T6 and T24, but the differences were not significant $(P > 0.10)$.

3.3 Stream Flow During Treatment Periods

Flows were monitored to evaluate how variations might influence treatment effects. Temporal flow patterns varied somewhat among streams due to differences in watershed size, slope, aspect, and other characteristics, but the patterns were generally comparable due to the close proximity of the streams. The flow record for T8 is presented to illustrate patterns of flow in relation to the treatment schedule of liming (Fig. [6](#page-8-0)). Flow regimes differed considerably among streams after the various lime applications. Following the first channel liming on 7/12/2012, base flows remained low and high-flow events were nominal through the rest of the summer. In contrast, after the 6/19/2013 treatment, discharge was elevated for several weeks. The lime additions on 2/28/14 in T6 and 3/5/ 2014 in T8 were specifically timed to precede the sustained high snowmelt flows that usually occur during early spring of most years. The maximum flow for the entire monitoring period (2012–2015) was observed during the 2014 snowmelt (Fig. [6\)](#page-8-0), and elevated flows continued through the summer of 2014. The channel liming on 6/16/2015 was followed by a short period of elevated flow, after which normal low summer flows occurred. The whole-watershed liming was followed by a series of high flows that continued into early winter in 2013, which was followed by high sustained snowmelt flows during spring 2014, and frequent high-flow epi-sodes in the summer of 2014 (Fig. [6\)](#page-8-0).

3.4 Chemical Responses to Lime Additions

Whole-watershed liming caused rapid and pronounced effects on stream chemistry in T16. Values of pH and ANC increased, and Alim concentrations decreased during the first few weeks after the helicopter lime application (Fig. [3](#page-6-0)). After this short period, pH and ANC stabilized at levels lower than the initial response, but well above pre-treatment means and values of the reference watershed T24. The watershed application decreased Alim to concentrations near or below the harmful threshold of 2.0 µmol L^{-1} for most of the posttreatment period. However, Alim concentrations elevated above the 2.0-µmol L^{-1} threshold were measured

Table 2 The means and ranges of daily stream temperatures during July and August of 2013, 2014, and 2015, and the means and ranges of silicon and sodium concentrations from samples collected on 7/19/2011, 8/1/2011, and 7/9/2012 at 5 study sites prior to liming. Mean values with different subscripts are statistically different $(P < 0.05$; Tukey multiple comparison test)

The mean values with different superscript letters are signifcantly different from each other at a decison level of 0.05

during snowmelt and early summer in 2015. Comparison between T16 and T24 indicated that the treatment had a strong effect in dampening seasonal variations in the measurements of all three constituents, which continued to be strongly expressed in T24 during the treatment period.

The response to the first lime addition in T8 on 7/12/ 2012 resulted in rapid and pronounced ANC and pH increases relative to levels before treatment and mea-surements at site T8A upstream of the addition (Fig. [4\)](#page-7-0). These high levels were sustained through the summer during low (base) flows and several minor flow events. By fall, pH and ANC concentrations at T8 had begun to approach those measured upstream of the lime addition at T8A and by spring snowmelt in 2013, values at T8 were similar to those upstream. Concentrations of Al_{im} remained similar to pre-treatment levels throughout the summer, but then decreased and remained low until the next application on 6/19/2013 (Fig. [4\)](#page-7-0). Within the first few weeks of the second treatment at T8, pH and ANC concentrations increased to levels similar to the peaks observed after the first treatment, but then decreased to

Fig. 6 Average daily flow measured in T8 from $1/1/2012$ through 12/31/2015. Vertical red lines indicate the dates of channel liming; dashed red line indicates the date of watershed liming at T16

concentrations approaching those at T8A, as seen in response to the first treatment. Concentrations of Alim at T8 after the second treatment were usually lower than those at T8A, and only one sample exceeded 2.0 µmol L^{-1} between the second and third treatments. Following the third treatment on 3/5/2014, pH and ANC concentrations at T8 remained higher than those observed upstream of the addition, but did not reach the peaks observed after the first two treatments. Concentrations of Alim generally remained below values at T8A, and only two samples exceeded 2.0 μ mol L⁻¹. The changes in pH, ANC, and Al_{im} concentrations following the fourth treatment on 6/16/2015 were comparable with the responses observed during the three prior treatments.

The addition of lime to T6 prior to this study in fall 2010 did not appear to have a strong effect on water chemistry by the fall of 2012; based on reported water chemistry from spring 2008 to spring 2010 (Josephson et al. 2014) and the pre-treatment pH, ANC, and Al_{im} data from the present study (Fig. [5](#page-7-0)). The chemical responses to the four treatments in T6 (Fig. [5](#page-7-0)) were comparable with those observed in T8 (Fig. [4](#page-7-0)). The largest increases in pH and ANC concentrations occurred in the weeks immediately following each treatment, with a gradual decrease until the next treatment. Increases in pH at T6 were similar to T8, but maximum levels of ANC were less than those observed at T8. Throughout the treatment period, concentrations of ANC and pH at T6 remained above those observed prior to treatment and at site T6A upstream of the addition. Highest concentrations of Al_{im} at T6 reached to nearly 5.0 μmol L^{-1} prior to the first lime treatment but decreased to less than 2.0 μ mol L⁻¹ in nearly all samples collected thereafter (Fig. [5](#page-7-0)).

3.5 Brook Trout Population Assessments

Summer Tributary Electrofishing Catch A total of 1410 brook trout and no other species were collected by backpack electrofishing from the five study tributaries during August surveys between 2009 and 2015. The catch consisted of 1314 brook trout with lengths < 100 mm and 96 trout ≥ 100 mm. Using length-frequency distributions of all fish (Fig. [7\)](#page-10-0), those brook trout less than 100 mm (93.2% of the total catch) were assumed to be age 0 and designated YOY. Thirty-nine of the 40 fish < 100 mm aged using otoliths were found to be age 0, which confirmed the 100-mm cut-off length for YOY.

The density of brook trout varied considerably among all five study streams before liming was initiated, as did their responses to liming of T6, T8, and T16 (Figs. [7](#page-10-0) and [8](#page-11-0)). Brook trout populations in the two untreated reference reaches were the most divergent. In chronically acidified reference stream T24, no brook trout were captured during the five pre-liming (2009–2013) or two post-liming (2014–2015) surveys. In contrast, large numbers of brook trout were collected at the rarely acidic reference stream T20 during the pre-liming (2009–2012) and post-liming (2013–2015) surveys. The mean density of YOY brook trout in the reference reach T20 increased 22%, from 1.04 fish/m² during the pre-lime period to 1.27 fish/m² during the post-lime period (Fig. [8\)](#page-11-0).

The effects of watershed liming at T16 were assessed through a comparison of YOY brook trout density with reference stream T24 before and after the 2013 aerial application. Brook trout density at T16 was very low before (mean density 0.02 fish/ $(m²)$ and after (mean density 0.03 fish/ $m²$) watershed liming, with no fish captured during most surveys. The BACI analysis comparing density of YOY brook trout at T16 and T24 did not indicate a significant effect of watershed liming $(F = 0.11, P =$ 0.756, BACI contrast = 0.012 , $SE = 0.037$).

The effects of channel liming at T6 and T8 were assessed through the comparison of two study reaches on each stream with the rarely acidic reference stream T20. A trivial increase in the mean density of YOY brook trout occurred near the confluence of T6.1 with Honnedaga Lake (0.05 fish/m^2) before liming to 0.07 fish/m² after liming; Fig. [8](#page-11-0)). The BACI analysis comparing density of YOY brook trout at T6.1 with that of T20 did not indicate a significant effect of channel liming $(F = 0.10, P = 0.768, BACI$ contrast = -0.204 , $SE = 0.653$). The density of YOY brook trout at T6.2 increased from 0.01 fish/m² before liming to 0.06 fish/ $m²$ after liming (Fig. [8\)](#page-11-0). The BACI analysis comparing density of YOY brook trout at T6.2 with that of T20 also did not indicate a significant effect of channel liming $(F = 0.05, P = 0.837, BACI$ contrast = $-0.160, SE =$ 0.731). The mean density of YOY brook trout at T8.1, near the confluence with the lake, increased from 0.4 fish/ $m²$ before liming to 2.7 fish/ $m²$ after liming (Fig. [8\)](#page-11-0). The BACI analysis comparing density of YOY brook trout at T8.1 with that of T20 indicated a significant effect of channel liming $(F = 18.44, P =$ 0.008, BACI contrast = 2.10, $SE = 0.488$). The mean density of YOY brook trout at T8.2 further upstream from the lake increased from 0.1 fish/ $m²$ before treatment to 0.5 fish/m² after treatment. The BACI analysis comparing density of YOY brook trout at T8.2 with that of T20 did not indicate a significant effect of channel liming $(F = 0.04, P = 0.846, BACI$ contrast = 0.158, $SE = 0.767$.

Fall Trap Net Catch The fall trap net data indicate that the mean catch rates of adult brook trout increased from 11 fish/net night between 2008 and 2010 up to 20 fish/ net night between 2011 and 2014 (Table [3](#page-11-0)). The lowest mean catch rate occurred in 2009 (8.2 fish/net night) and the highest occurred in 2014 (25.9 fish/net night).

Fall Redd Counts Total redd counts in the Honnedaga Lake watershed (outlet, tributaries, and shoals) increased significantly between 2008 and 2014 (linear regression; $R^2 = 0.64$, $P = 0.03$) (Table [4\)](#page-12-0). However, the trends in redd counts in the three limed tributaries (T6, T8, T16), the reference site T20, and the two additional spawning locations at T4 and Jock's Falls shoal, did not change over the same period. The lake outlet and associated shoals were the only areas that changed significantly, increasing from 7 redds in 2008 to 60 redds in 2014 (linear regression; $R^2 = 0.80$, $P < 0.01$). This finding indicates the increasing lakewide trend in redd counts was driven mainly by increased spawning at the outlet (and adjacent shoals) rather than a widespread increase at other spawning locations.

4 Discussion

The present study demonstrated that additions of lime once a year to the channels of streams undergoing

Fig. 7 Length frequency distribution of all brook trout captured during the first pass of summer (early August) electrofishing surveys done in tributaries to Honnedaga Lake annually (2009–

2015). Lime was applied to the channels of T6 and T8 each year from 2012 to 2015. Lime was applied to the T16 watershed in fall 2013

frequent episodic acidification were effective at creating chemical conditions suitable for reproducing brook trout populations. Harmful levels of acidity between treatments were highly infrequent, occurring less often than in the rarely acidic reference stream that supported a natural population of reproducing brook trout. This included treatment effects that extended through the 15-month interval from late February–early March 2014 to mid-June 2015. Notably, the liming in late winter 2014 provided effective acid neutralization through a sustained period of high-flow snowmelt, as well as through unseasonably high flows during the following summer. The single whole-watershed liming of chronically acidic T16 also created chemical conditions over the 2-year post-treatment period that were likely to be suitable for a reproducing brook trout population, although this stream was somewhat more acidic than T6 or T8 following treatment. The acid neutralization was likely the result of lime that fell in or near the stream channel. A period longer than 2 years after treatment would likely be required before large changes in stream chemistry would occur via changes in soils.

The start of liming treatments in 2012 coincided with a large YOY increase in T8 that began in 2013, a result that suggested liming contributed to this increase in YOY brook trout. However, YOY brook trout can

Fig. 8 The density of YOY brook trout captured in the first pass of summer (early August) electrofishing surveys done at seven study sites in five tributaries to Honnedaga Lake annually (2009– 2015). (The open bars denote brook trout densities prior to liming and the shaded bars denote brook trout densities after liming.) Lime was applied to the channels of T6 and T8 each year from 2012 to 2015. Lime was applied to the T16 watershed in fall 2013

disperse from spawning areas around lake shorelines in the spring and move into cooler groundwater-fed tributaries as lake surface temperatures increase in late spring and early summer (Curry et al. [1995;](#page-13-0) Biro et al. [1997\)](#page-13-0). Numerous redds occurred within T8 and on a nearby shoal in the lake, but there was no trend in the number of redds from 2008 to 2014 to suggest an increase in spawning within this area. In fact, the only location with a significant increase in the number of redds $(P < 0.01)$ during the treatment period was in and near the lake outlet. Movement of YOY from the outlet area along shorelines could potentially increase numbers of YOY in tributary streams. However, reference T20, which was about 0.94 km from the outlet area, showed decreases in numbers of YOY in 2013 and 2014 relative to 2012, whereas spawning near the lake outlet increased

Table 3 The mean and ranges of brook trout catch rates (number per net night) from fall (October) trap net surveys at six sites in Honnedaga Lake annually (2008 to 2014)

Year	Trap net CPUE (number per net night)				
	Mean	Range			
2008	14.2	13.0 to 22.0			
2009	8.2	$2.0 \text{ to } 20.3$			
2010	11.9	0.7 to 19.3			
2011	19.7	8.0 to 37.7			
2012	20.8	10.0 to 42.7			
2013	14.7	1.0 to 30.3			
2014	25.9	8.7 to 38.3			

substantially in 2013 and 2014 relative to 2012. T8 was 1.6 km from the outlet area, so it would seem unlikely that the increased spawning in the outlet area would have had a large effect on YOY in T8. Furthermore, natural recovery from acidic deposition in T20 in terms of both stream chemistry and YOY numbers appeared to be stalled from 2012 to 2015. Comparison with T20 suggested that the response in T8 would not have occurred through natural recovery processes. The overall evidence points to liming as the most likely factor accounting for an increase in YOY brook trout recruitment in T8; a result that is also consistent with other stream-liming studies (Lawrence et al. [2016\)](#page-13-0).

The lack of an increase in YOY brook trout in T6 despite the successful neutralization of acidic water indicated that factors beyond water chemistry were limiting brook trout densities in this stream. The relatively low concentrations of Na and Si in T6 suggest a lack of subsoil groundwater inputs critical to brook trout spawning habitat in streams and lakes (Schofield [1993\)](#page-13-0). Concentrations of Si and Na were previously found to be higher in Adirondack lakes with reproducing brook trout populations than in those without natural reproduction (Schofield [1993\)](#page-13-0). We speculate that the greater groundwater inputs and associated spawning at T8 resulted in large cohorts of swim-up fry that benefited directly from improved spring and summer runoffevent chemistry. Comparable responses were observed in Woods Lake where, after liming two watersheds, brook trout successfully spawned in one tributary with large groundwater inputs, but not in another with only nominal groundwater inputs (Porcella et al. [1995;](#page-13-0) Schofield and Keleher [1996\)](#page-14-0). Maximum summer water temperatures in T6 may also have been limiting. Upstream wetlands within the T6 watershed undoubtedly contributed to summertime water temperatures in excess of 20 °C, which did not occur in the watersheds of the other four study streams where little or no wetland development existed.

Concentrations of Si and Na in T16 were similar to T6, but low in comparison with T8 and T20, suggesting that low inputs of groundwater could also limit spawning in T16. The presence of chronic acidification in T16 also indicated that little or no input of water from subsoil flow paths buffers this tributary. Furthermore, T16 is isolated from the primary spawning shoals located 5.8 km away at T8 and 7.3 km away at the lake outlet. Together, these factors made T16 a poor candidate for liming to enhance brook trout reproduction.

Year	Redd count (number)									
	Outlet and shoal	Jock's Falls Shoal	T ₄	T ₆	T8 and shoal	T ₂₀ and shoal	Total			
2008		15	3	$\mathbf{0}$	23		48			
2009	9	13	6	$\mathbf{0}$	60	2	90			
2010	16	8	3	$\mathbf{0}$	39	23	89			
2011	20	θ	2	6	45	14	87			
2012	18	11			33	3	67			
2013	57	23	6	$\mathbf{0}$	35	23	144			
2014	60	16	5.	2	49	17	149			

Table 4 Brook trout redd counts (number) from fall (late October and early November) surveys at shoals, tributaries and the outlet within the Honnedaga Lake watershed (2008–2014)

5 Conclusion

Results of this study have a number of important implications for the protection and management of fisheries, understanding present-day effects of acid deposition, and development of targeted liming strategies to accelerate chemical and biological recovery in acidified streams and lakes across the Adirondack region and other regions where recovery from acidic deposition is occurring. The lack of a significant biological response to improved acid-base chemistry at four of the five study sites emphasized that biological recovery in acidified streams is also dependent on additional factors that affect reproductive success and recruitment (Warren et al. [2010\)](#page-14-0). The strong biological response to liming in T8 indicates that when other factors are not limiting to brook trout recruitment, liming of acidified streams can be a useful tool for augmenting trout densities in streams that have not fully recovered from acidic deposition.

Brook trout are one of the most acid-tolerant fish species in the region and this experiment was conducted in a lake with only this species. As such, it cannot be assumed that the chemical response achieved in T8 would be sufficient to promote recovery of other fish species and/or assemblages of multiple species with different life history requirements. Questions also remain regarding how liming affects the overall functioning of aquatic ecosystems that have begun to respond to acid deposition declines. A recent study of liming effects on macroinvertebrate communities in these same streams (George et al. [2018\)](#page-13-0) found that neither channel nor wholewatershed liming improved the condition of macroinvertebrate communities and may have had negative effects from rapid fluctuations in water chemistry and coating of channel substrate as lime particles settled in reaches with low flow rates. These results raise the question of how stream liming affects food webs and ecosystem structure, which will need to be addressed with long-term studies than the work presented here.

For the purpose of accelerating biological recovery of brook trout, liming strategies must take into account all relevant factors of life history and habitat, which include groundwater quality and quantity, thermal conditions, and the recovery trajectory of stream chemistry. Liming of streams such as T6, which did not meet the necessary conditions for sustaining productive brook trout populations, would not be useful for improving brook trout numbers, but improvements in stream chemistry might be considered useful in accelerating recovery of other biological targets. Streams that show a strong recovery trajectory in chemical conditions that could remove limits to brook trout recruitment in the near future would not be considered a high priority for liming.

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Compliance with Ethical Standards

Disclaimer Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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